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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention a hard carbon film like diamond like carbon ("DLC" is called hereafter) to a sliding surface with respect to the low friction sliding material which it had, for example more particularly, It is suitable for the use in an internal-combustion engine etc., and is related with the hard carbon film slide member which shows the low friction nature which was extremely excellent under existence of lubricating oils, such as an engine oil and transmission oil.

[0002]

[Description of the Prior Art]

A close-up of global environmental problems, such as warming of the whole earth and depletion of an ozone layer, is taken greatly, and big concern is attracted in each country involving how to decide the restriction value about CO₂ reduction said to especially have big influence on warming of the whole earth.

About CO₂ reduction, it is one of the big technical problems to aim at reduction of the fuel consumption of a car, and the role which a sliding material and a lubricating oil play is large.

[0003]

The role of a sliding material is excelling in abrasion resistance and revealing a low coefficient of friction to the part where friction wear environment is cruel, in an engine sliding part.

These days, application of various hard thin film materials including DLC material is progressing.

Since the coefficient of friction under [, such as inside of the air,] the environment where a lubricating oil does not intervene is generally low compared with the hard coating material of

abrasion resistance, such as TiN and CrN, the DLC material as a hard thin film is expected as a low friction sliding material. However, it is known that the friction reduction effect is not necessarily large under lubricating oil existence although such a common DLC material is excellent in the air at low friction nature (refer to nonpatent literature 1).

[0004]

On the other hand, in order to prevent this as parts for internal-combustion engines since it becomes easy to generate printing by agglutination of metal if the same metal is contained in the sliding surface of the both sides of a cylinder bore piston skirt part, for example, For example, in order to form a resin coating layer in the piston skirt part surface and to improve the sliding characteristic of the enveloping layer concerned, Molybdenum disulfide which is a solid lubricant at polyamidoimide (PAI) resin as a binding material, or polyimide (PI) resin (MoS_2), Covering the coating agent which added polytetrafluoroethylene (PTFE), graphite, etc. is performed (for example, refer to patent documents 1).

[0005]

[Nonpatent literature 1]

The Japanese Society of Tribologists [besides Kano] proceedings, May, 1999, p.11-12

[Patent documents 1]

JP,7-97517,A

[0006]

[Problem(s) to be Solved by the Invention]

However, coating which consists of resin indicated to the above-mentioned patent documents 1 and a solid lubricant is performed in order to improve the sliding characteristic between a piston and a cylinder bore, but. Abrasion resistance is not necessarily enough on the strength property of resin, and there is room for an improvement about the point of maintaining the early characteristic.

Only with namely, the resin layer formed on the striation of a piston skirt part. In sliding with a mating material since the function in which the shape where the early striation was imitated by wear changes with wear of a sliding part, and carries a lubricating oil in connection with the passage of time falls, Although the improvement of the friction characteristic was made by addition of the solid lubricant to the inside of a resinous principle, it was not necessarily enough and dissolution of such a problem had become a technical problem in the conventional slide member which performed coating which consists of resin and a solid lubricant.

[0007]

There is a place which this invention is made that the aforementioned problem in the conventional slide member should be solved, and is made into the purpose in providing the hard carbon film slide member which can improve the friction characteristic of the outermost surface substantially, harnessing the characteristic which is rich in the elasticity of a resin

material.

[0008]

[Means for Solving the Problem]

That this invention persons should attain the above-mentioned purpose A kind and the characteristic of a hard carbon film, The physical properties of a substrate which forms the hard carbon film concerned, a result of having repeated examination wholeheartedly about a lubricating oil, its additive, etc. further, To a part on which it slides via a mating material and a lubricating oil in a substrate which comprises steel materials or an aluminum material. By making with an interlayer an elastic layer which comprises addition particles a resin material or a resin material, and forming hard carbon films, such as DLC, in the surface of the interlayer concerned further, for example, it finds out that an aforementioned problem is solved and came to complete this invention.

[0009]

That is, a hard carbon film slide member of this invention is a slide member which slides under existence of a lubricating oil, uses steel materials or an aluminum material as a substrate, and is characterized by equipping a sliding part with a mating material with a hard carbon film via an interlayer who comprises resin which has rubber or the melting point of not less than 150 **.

[0010]

[Embodiment of the Invention]

Hereafter, this invention is explained in detail. Mass percentage shall be shown unless it mentions specially "%" in this specification.

The hard carbon film slide member of this invention via the elastic interlayer who becomes a sliding surface of the substrate which comprises a steel material, an aluminum material, etc. from rubber, resin, etc. as mentioned above, Give hard carbon covering of DLC material etc. and the flattery nature to the mating member in a sliding part improves by existence of the interlayer excellent in elasticity, Since a touch area increases and planar pressure is maintained low, the abrasion resistance of the hard carbon film of the outermost superficial layer and the low friction characteristic will decrease [a coefficient of friction and abrasion loss] substantially conjointly.

[0011]

Here, as the above-mentioned hard carbon film material, the DLC material mainly constituted in a carbon element can be used. This DLC material is amorphous and the connection form of carbon comprises both diamond structure (SP³ combination) and graphite combination (SP² combination). Although MeC which specifically contains in part metallic elements, such as a-C (amorphous carbon) which comprises only a carbon element, a-C:H (hydrogen amorphous carbon) containing hydrogen and titanium (Ti), and molybdenum (Mo), is mentioned, In this

invention, fewer things have the viewpoint of demonstrating a large friction reduction effect as the above-mentioned DLC material to a more preferred hydrogen content, and it is preferred that a hydrogen content is 0.5% or less in an atomic ratio. In this case, it is also possible to make a coated layer into two-layer or the multilayer structure beyond this, and to make it the hydrogen content of the outermost layer become from a viewpoint of decreasing preponderantly hydrogen of the outermost surface of a hard carbon film layer below in 0.5 atom %.

[0012]

PVD, a CVD method, sputtering process, etc. which are publicly known thin film coating technology are applied to formation of such a hard carbon film layer -- it can carry out, and especially according to the PVD, a hard carbon film layer with a low hydrogen content can be formed. Therefore, if it faces forming the coated layer of the above multilayer structure, the lower layer side coated layer is formed with a CVD method and membranes are formed by PVD about the top layer, hydrogen quantity of the outermost surface can be made for example, into the following [0.5 atom %].

It is preferred that the coating thickness of a hard carbon film is 0.3-2.0 micrometers. That is, if it will wear out and become easy to carry out if the coating thickness of a hard carbon film is set to less than 0.3 micrometer, and coating thickness exceeds 2.0 micrometers, it will be because there is a tendency to become easy to exfoliate from the brittleness characteristic.

[0013]

As a material which constitutes the above-mentioned interlayer, a not less than 150 ** resin material is used for rubber or the melting point. The melting point uses not less than 150 ** resin, in order that the temperature of the engine oil used for the internal-combustion engine of a car may reach 150 **. It is independent or, specifically, polyamidoimide (PAI), polyimide (PI), rubber, a polyether ether ketone (PEEK), polyamide (PA), etc. can be used, for example, combining these two or more sorts arbitrarily.

[0014]

It can add to the above-mentioned interlayer, combining independently or arbitrarily a particulate additive (MoS₂), for example, molybdenum disulfide, tetrafluoroethylene (PTFE), black lead (graphite), etc., and he can maintain mu characteristic at the time of film peeling by this.

It is desirable to consider it as the range of about 5-20 micrometers from a viewpoint of reducing the planar pressure of a contact portion, as an interlayer's thickness.

[0015]

The hard carbon film slide member of this invention is excellent in the scuff-proof nature to aluminum, and the further effect is acquired when the member which comprises an aluminum material is a mating material. For example, in order to avoid sliding of ** material with

aluminum of the piston skirt from a viewpoint of scuff-proof nature, there is an example using the resin layer which distributed the flake made from iron plating or stainless steel, but as compared with these, low friction is obtained more for the DLC film.

[0016]

The hard carbon film slide member of this invention can be applied, for example to the piston of an internal-combustion engine, and an interlayer and a hard carbon film are formed in their striation processing superiors in a piston skirt part in this case, Namely, the height and pitch of a striation processing eye which were formed at right angles to the sliding direction of a piston in order to give the conveyance function of a lubricating oil to a piston skirt part are received, When it secures the conveyance function of a lubricating oil that unevenness by a striation processing eye is made not to be lost on the hard carbon film surface after membrane formation of an interlayer and a hard carbon film layer as an interlayer and hard carbon film layer thickness will not become extremely thick, it is desirable.

[0017]

As for the hard carbon film slide member of this invention, it is desirable to be able to apply also to the bearing-metal parts for internal-combustion engines, and to form an interlayer and a hard carbon film like the case of the above-mentioned piston, also in this case, so that unevenness by a striation processing eye may not be lost by its striation processing superiors of a sliding surface.

[0018]

Next, the lubricating oil composition used for this invention is explained in detail.

As a lubricating oil used for this invention, what makes lubricant base oil contain a fatty-acid-ester system ash-free friction modifier and/or a fatty amine system ash-free friction modifier, and grows into it can be used conveniently.

[0019]

Here, if it is not limited especially as the above-mentioned lubricant base oil and normal use is carried out as base oil of lubricating oil compositions, such as mineral oil, synthetic oil, fats and oils, and these mixtures, it can be used regardless of a kind.

As mineral oil, atmospheric distillation and the lubricating oil fraction produced by carrying out distillation under reduced pressure for a crude oil specifically Solvent deasphalting, Although oils refined combining suitably purification treatment, such as solvent extraction, hydrocracking, solvent dewaxing, hydrorefining, sulfuric acid treatment, and clay treatment, etc., such as paraffin series or a naphthene system, normal paraffin, etc. can be used and solvent refining and the thing which carried out hydrorefining processing are common, It is more preferred to use what was manufactured by the technique of having isomerized the advanced hydrocracking process and GTL Wax (Gastaut liquid wax) which can reduce a part for aromatic series more.

[0020]

as synthetic oil -- concrete -- the Polly alpha olefin (for example, 1-octene oligomer.) The hydride of Polly alpha olefins, such as 1-decene oligomer and an ethylene-propylene oligomer, The hydride of isobutene oligomer and isobutene oligomer, isoparaffin, alkylbenzene, alkyl naphthalene, and diester (for example, a ditridecyl GURUTA rate.) Dioctyl adipate, di-isodecyl adipate, a ditridecyl horse mackerel peat, polyol esters (for example, a trimethylolpropane KAPURI rate.), such as dioctyl sebacate Trimethylolpropanester, such as trimethylolpropane pelargonate and trimethylolpropaniso steer RINETO; Pentaerythritol 2-ethylhexanoate, Pentaerythritol ester, such as pentaerythritol pelargonate, polyoxy alkylene glycol, dialkyl diphenyl ether, a polyphenyl ether, etc. are mentioned. Especially, Polly alpha olefins, such as 1-octene oligomer and 1-decene oligomer, or the hydride of those is mentioned as a desirable example.

[0021]

Besides independent, mixing and using, even if the base oil in the lubricating oil composition used for this invention is a mixture of two or more kinds of mineral oil system base oil, or two or more kinds of constructional system base oil, it does not interfere mineral oil system base oil or constructional system base oil. The mixture ratio in particular of two or more kinds of base oil in the above-mentioned mixture is not limited, either, but it can choose arbitrarily.

[0022]

Although there is no restriction in particular about the sulfur content in lubricant base oil, it is a base oil whole-quantity standard, and it is preferred that it is 0.2% or less, and it is preferred that they are 0.1% or less and 0.05 more% or less more preferably. As for especially the sulfur content of hydrotreating mineral oil or constructional system base oil, 0.005% or less or since sulfur content is not contained substantially (5 ppm or less), it is preferred to use these as base oil.

[0023]

Although there is no restriction in particular also about the aroma content in lubricant base oil, in order to maintain the prolonged low friction characteristic as an internal-combustion-engine-oil constituent, it is preferred that all the aromatic content is 15% or less, and it is preferred that they are 10% or less and 5 more% or less more preferably. That is, when all the aromatic content of lubricant base oil exceeds 15%, since oxidation stability is inferior, it is not desirable.

All the aromatic content said here means the aromatic fraction (aromatics fraction) content measured based on the method specified to ASTM D2549.

[0024]

Although there is no restriction in particular also in the kinetic viscosity of lubricant base oil, when using it as an internal-combustion-engine-oil constituent, it is preferred that the kinetic

viscosity at 100 ** is more than $2\text{-mm}^2/\text{s}$, and it is more than $3\text{-mm}^2/\text{s}$ more preferably. On the other hand, as for the kinetic viscosity, it is preferred that it is below $20\text{-mm}^2/\text{s}$, and it is [below $10\text{ mm}^2/\text{s}$] especially preferred that it is below $8\text{-mm}^2/\text{s}$. When the kinetic viscosity at 100 ** of lubricant base oil is less than $2\text{-mm}^2/\text{s}$, since sufficient abrasion resistance is not obtained and also an evaporation characteristic may be inferior, it is not desirable. On the other hand, since it is hard to demonstrate low friction performance and low-temperature performance may worsen when kinetic viscosity exceeds $20\text{-mm}^2/\text{s}$, it is not desirable. In this invention, in the limitation which can use the mixture etc. which mixed arbitrarily two or more sorts of base oil chosen from the above-mentioned base oil and by which the kinetic viscosity at 100 ** enters within the limits of [desirable] the above, even if base oil independent kinetic viscosity is things other than the above, it is usable.

[0025]

Although there is no restriction special also to the viscosity index of lubricant base oil, it is preferred that it is 80 or more, it is still more preferred that it is 100 or more, and when using it especially as an internal-combustion-engine-oil constituent, it is preferred that it is 120 or more. There are few oil consumptions by raising the viscosity index of lubricant base oil, and the internal-combustion-engine-oil constituent excellent in the low-temperature-viscosity characteristic and the fuel-efficient performance can be obtained.

[0026]

As the above-mentioned fatty-acid-ester system ash-free friction modifier and/or a fatty amine system ash-free friction modifier, the carbon numbers 6-30 -- the carbon numbers 8-24, the fatty acid ester which has the straight chain shape or the letter hydrocarbon group of branching of the carbon numbers 10-20 preferably especially, fatty acid amine compounds, and these arbitrary mixtures can be mentioned preferably. When a carbon number is outside the range of 6-30, a friction reduction effect may not fully be acquired.

[0027]

As the straight chain shape or the letter hydrocarbon group of branching of the carbon numbers 6-30, Pass and specifically A KISHIRU group, a heptyl group, an octyl group, a nonyl group, a decyl group, An undecyl group, the dodecyl, a tridecyl group, a tetradecyl group, a pentadecyl group, A hexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, An icosyl group, a henicoyl group, a docosyl group, a tricosyl group, a tetracosyl group, A pentacosyl group, a hexacosyl group, a heptacosyl group, an octacosyl group, Alkyl groups, such as a nonacosyl group and a triacontyl group, a hexenyl group, a heptenyl group, An octenyl group, a nonenyl group, a decenyl group, an undecenyl group, a dodecenyl group, A tridecenyl group, a tetra decenyl group, a penta decenyl group, a hexa decenyl group, A heptadecenyl group, an octadecenyl group, a nona decenyl group, an icosenyl group, Alkenyl

groups, such as a henicosenyl group, a docosenyl group, a tricosenyl group, a tetracosenyl group, a pentacosenyl group, a hexacosenyl group, a heptacosenyl group, an octacosenyl group, a nonacosenyl group, and a triacontenyl group, etc. can be mentioned.

All the straight-chain-shape structures and letter structures of branching which are considered are included in the above-mentioned alkyl group and an alkenyl group, and the position of the double bond in an alkenyl group is arbitrary.

[0028]

As the above-mentioned fatty acid ester, ester with fatty acid and aliphatic series monohydric alcohol which have a hydrocarbon group of these carbon numbers 6-30, or aliphatic polyhydric alcohol, etc. can be illustrated, Specifically, glycerin mono- olate, glycerin diolate, sorbitan mono- olate, sorbitan diolate, etc. can be especially mentioned as a desirable example.

As the above-mentioned fatty amine compound, these derivatives, such as aliphatic series monoamine or its alkylene oxide addition, aliphatic polyamine, and an imidazoline compound, can be illustrated. Specifically Lauryl amine, lauryl diethylamine, lauryl diethanolamine, Dodecyl dipropanolamine, palmitylamine, stearylamine, Stearyl tetraethylenepentamine, oleylamine, oleylpropylenediamine, Fatty amine compounds, such as oleyldiethanolamine and N-hydroxyethyl oleylimidazoline, Amine alkylene oxide additions, such as N,N-dipolyoxyalkylene N-alkyl (or alkenyl) (carbon numbers 6-28) of these fatty amine compound, To these fatty amine compound, the monocarboxylic acid (fatty acid etc.) of the carbon numbers 2-30, What is called an acid denaturation compound etc. that the polycarboxylic acid of the carbon numbers 2-30 of oxalic acid, phthalic acid, trimellitic acid, pyromellitic acid, etc. was made to act, and neutralized a part or all of the amino group and/or imino group which remain, or were amidated are mentioned. N,N-dipolyoxy ethylene-N-oleylamine etc. are mentioned as a suitable example.

[0029]

The content of the fatty-acid-ester system ash-free friction modifier contained in the lubricating oil composition used for this invention and/or a fatty amine system ash-free friction modifier, Although there is no restriction in particular, it is a constituent whole-quantity standard, and it is desirable still more preferred that it is 0.05 to 3.0%, and it is good that it is 0.5 to 1.4% especially preferably 0.1 to 2.0%. Since the solubility to a lubricating oil and storage stability will get worse remarkably and it will be easy to generate a sediment if a friction reduction effect becomes it small easily that the above-mentioned content is less than 0.05% and it exceeds 3.0%, it is not desirable.

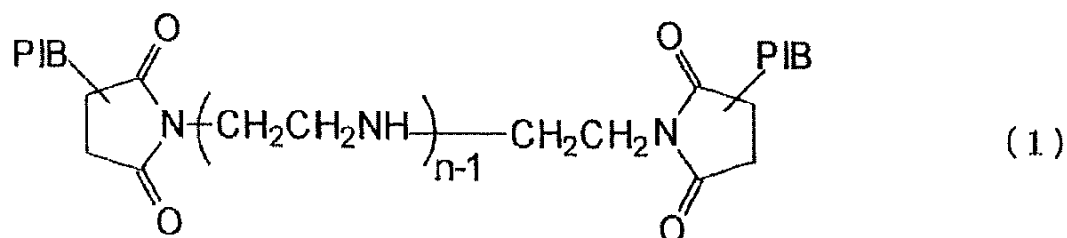
[0030]

It is preferred for the lubricating oil composition used for this invention on the other hand to contain polybutenyl succinimid and/or its derivative.

General formula [following] (1) Reach as the above-mentioned polybutenyl succinimid (2).

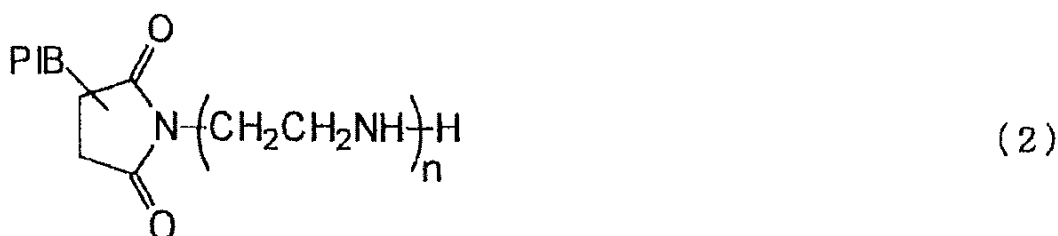
[0031]

[Formula 1]



[0032]

[Formula 2]



It comes out and a compound expressed is mentioned. PIB in these general formulas shows a polybutenyl group, a number average molecular weight produced by polymerizing a mixture of high purity isobutene or 1-butene, and isobutene with a boron fluoride system catalyst or an aluminum chloride series catalyst -- 900-3500 -- it is desirably obtained from polybutene of 1000-2000. Since the detergency effect is inferior easily when the above-mentioned number average molecular weight is less than 900, and it is easy to be inferior to cold-temperature fluidity when exceeding 3500, it is not desirable.

As for n in the above-mentioned general formula, it is good an integer of 1-5 and that it is an integer of 2-4 more desirably from a point of excelling in a detergency. The above-mentioned polybutene is also good to use them 10 ppm or less more desirably, 50 ppm or less, by suitable methods, such as an adsorption process and sufficient rinsing, after removing especially desirably a little parts for a part for fluoride, or chlorine which originate in a catalyst of a manufacturing process and remain to 1 ppm or less.

[0033]

As a manufacturing method of the above-mentioned polybutenyl succinimid, Although there is

no limitation in particular, a chlorination thing or chlorine of the above-mentioned polybutene, and fluoride polybutenyl succinic acid produced by making polybutene and a maleic anhydride which were removed enough react at 100-200 **, for example, It can obtain by making it react to polyamine, such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine.

[0034]

On the other hand, as a derivative of the above-mentioned polybutenyl succinimid, A boron compound and an oxygenated organic compound are made to act on a compound expressed with the ***** type (1) or (2), a part or all of an amino group and/or an imino group which remain can be neutralized, or amidated what is called boron denaturation or an acid denaturation compound can be illustrated. Boron content polybutenyl succinimid, especially boron content screw polybutenyl succinimid are mentioned as most desirable thing also in it.

[0035]

As the above-mentioned boron compound, boric acid, borate salt, the ester of boric acid, etc. are mentioned. Specifically, orthoboric acid, metaboric acid, tetraboric acid, etc. are mentioned as the above-mentioned boric acid. As the above-mentioned borate salt, ammonium pentaborate, such as metaboric acid ammonium, tetraboric acid ammonium, 5 ammonium pentaborate, and 8 ammonium pentaborate, is mentioned to concrete targets, such as ammonium salt, as a good example, for example. moreover -- as the ester of boric acid -- boric acid -- desirable -- ester with alkyl alcohol of the carbon numbers 1-6 -- more specifically. Boric acid monomethyl, boric acid dimethyl, trimethyl borate, boric acid monoethyl, boric acid diethyl, boric acid triethyl, boric acid monopropyl, boric acid dipropyl, boric acid TORIPU propyl, boric acid monobutyl, boric acid dibutyl, tributyl borate, etc. are mentioned as a good example. Mass ratios "B/N" of boron content B and the nitrogen content N in boron content polybutenyl succinimid are usually 0.1-3, and are 0.2-1 preferably.

As the above-mentioned oxygenated organic compound, specifically, For example, formic acid, acetic acid, glycolic acid, propionic acid, lactic acid, butanoic acid, a valeric acid, Caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, Undecylic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, Pulmitic acid, margaric acid, stearic acid, oleic acid, nonadecanoic acid, Monocarboxylic acid of the carbon numbers 1-30 of eicosanoic acid etc., and oxalic acid, phthalic acid, Poly KARUPON acid of the carbon numbers 2-30 of trimellitic acid, pyromellitic acid, etc. and these anhydrides or an ester compound, alkylene oxide of the carbon numbers 2-6, hydroxy (poly) oxyalkylene carbonate, etc. are mentioned.

[0036]

In a lubricating oil composition used for this invention, although content in particular of polybutenyl succinimid and/or its derivative is not restricted, 0.1 to 15% is desirable and it is preferred that it is 1.0 to 12% more desirably. At less than 0.1%, if it may become deficient in

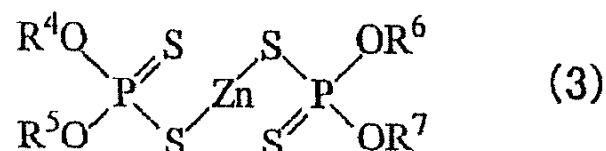
the detergency effect and exceeds 15%, the detergency effect of balancing content will be hard to be acquired, and demulsibility will get worse easily.

[0037]

A lubricating oil composition used for this invention is the following general formula (3) again.

[0038]

[Formula 3]



It is preferred to come out and to contain the dithiophosphate zinc expressed.

R^4 , R^5 , R^6 , and R^7 in the above-mentioned formula (3) show the hydrocarbon group of the carbon numbers 1-24 separately, respectively. As these hydrocarbon groups, the alkyl group of the straight chain shape of the carbon numbers 1-24, or the letter of branching, The alkyl cycloalkyl group of the alkenyl group of the straight chain shape of the carbon numbers 3-24, or the letter of branching, the cycloalkyl group of the carbon numbers 5-13, straight chain shape, or the letter of branching, It is desirable that it is arylated alkyl either an alkyl aryl group of the aryl group of the carbon numbers 6-18, straight chain shape, or the letter of branching or a group of the carbon numbers 7-19, etc. An alkyl group and an alkenyl group may be any of the 1st class, the 2nd class, and the 3rd class.

[0039]

As the above-mentioned R^4 , R^5 , R^6 , and R^7 , Specifically A methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, Pass and A KISHIRU group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, The dodecyl, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, A heptadecyl group, an octadecyl group, a nonadecyl group, an icosyl group, a hencicosyl group, Alkyl groups, such as a docosyl group, a tricosyl group, and a tetracosyl group, a propenyl group, An isopropenyl group, a butenyl group, a butadienyl group, a pentenyl group, a hexenyl group, A heptenyl group, an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, A dodecenyl group, a tridecenyl group, a tetra decenyl group, a penta decenyl group, Octadecenyl groups, such as a hexa decenyl group, a heptadecenyl group, and an oleyl group, A nona decenyl group, an icosenyl group, a hencosenyl group, a docosenyl group, Cycloalkyl groups, such as alkenyl groups, such as a tricosenyl group and a tetracosenyl group, a cyclopentyl group, a

cyclohexyl group, and a cycloheptyl group, a methyl cyclopentyl group, a dimethyl cyclopentyl group, an ethyl cyclopentyl group, a propyl cyclopentyl group, An ethylmethyl cyclopentyl group, a trimethyl cyclopentyl group, a diethyl cyclopentyl group, An ethyldimethyl cyclopentyl group, a propylmethyl cyclopentyl group, A propylethyl cyclopentyl group, a di-propyl cyclopentyl group, A propylethyl methyl cyclopentyl group, a methyl cyclohexyl group, A dimethyl cyclohexyl group, an ethyl cyclohexyl group, a propyl cyclohexyl group, An ethylmethyl cyclohexyl group, a trimethyl cyclohexyl group, a diethyl cyclohexyl group, An ethyldimethyl cyclohexyl group, a propylmethyl cyclohexyl group, A propylethyl cyclohexyl group, a di-propyl cyclohexyl group, A propylethyl methylcyclohexyl group, a methyl cycloheptyl group, A dimethyl cycloheptyl group, an ethyl cycloheptyl group, a propyl cycloheptyl group, An ethylmethyl cycloheptyl group, a trimethyl cycloheptyl group, a diethyl cycloheptyl group, Alkyl cycloalkyl groups, such as an ethyldimethyl cycloheptyl group, a propylmethyl cycloheptyl group, a propylethyl cycloheptyl group, a di-propyl cycloheptyl group, and a propylethyl methyl cycloheptyl group, a phenyl group, Aryl groups, such as a naphthyl group, a tolyl group, a xylyl group, an ethyl phenyl group, A propyl phenyl group, an ethyl methylphenyl group, a trimethyl phenyl group, A buthylphenyl group, a propylmethyl phenyl group, a diethyl phenyl group, An ethyl dimethylphenyl group, a tetramethyl phenyl group, a pentyl phenyl group, A hexyl phenyl group, a heptyl phenyl group, an octyl phenyl group, a nonylphenyl group, Arylated alkyl groups, such as alkyl aryl groups, such as a decyl phenyl group, an undecyl phenyl group, and a dodecyl phenyl group, benzyl, a methylbenzyl group, a dimethylbenzyl group, a phenethyl group, a methylphenethyl group, and a dimethylphenethyl group, etc. can be illustrated.

To the above-mentioned hydrocarbon group which R^4 , R^5 , R^6 , and R^7 can take. All the straight-chain-shape structures and letter ***** of branching which are considered are contained, and a position of a double bond of an alkenyl group, a connecting position to a cycloalkyl group of an alkyl group, a connecting position to an aryl group of an alkyl group, and a connecting position to an alkyl group of an aryl group are arbitrary. Especially a case where it is an aryl group of the carbon numbers 6-18, straight chain shape, or a letter alkyl aryl group of branching also in the above-mentioned hydrocarbon group when the hydrocarbon group is an alkyl group of the carbon numbers 1-18 of straight chain shape or the shape of meristele is preferred.

[0040]

As a suitable example of the above-mentioned dithiophosphate zinc, For example, diisopropyl dithiophosphate zinc, diisobutyl dithiophosphate zinc, Di-sec-butyl dithiophosphate zinc, di-sec-pentyl dithiophosphate zinc, Di-n-hexyl dithiophosphate zinc, di-sec-hexyl dithiophosphate zinc, Zinc dioctyldithiophosphate, di-2-ethylhexyl dithiophosphate zinc, di-n-decyl dithiophosphate zinc, di-n-dodecyl dithiophosphate zinc, JIISO tridecyl dithiophosphate zinc, a

mixture concerning these arbitrary combination, etc. are mentioned.

[0041]

Although content in particular of the above-mentioned dithiophosphate zinc is not restricted, it is a constituent whole-quantity standard from a viewpoint and a phosphorus element equivalent unit which demonstrate a higher friction reduction effect, It is preferred that it is 0.1% or less, it is more preferred that it is 0.06% or less, and also especially a thing that dithiophosphate zinc does not contain is preferred. When content of dithiophosphate zinc exceeds 0.1% by a phosphorus element equivalent unit, there is a possibility that a friction reduction effect which was excellent in the above-mentioned fatty-acid-ester system ash-free friction modifier in a sliding surface of a DLC member and an iron base material or the above-mentioned fatty amine system ash-free friction modifier may be checked.

[0042]

Although a conventional method can be adopted arbitrarily and it is not restricted in particular as a manufacturing method of the above-mentioned dithiophosphate zinc, specifically, For example, it is compoundable by making alcohol or phenol with a hydrocarbon group corresponding to the above-mentioned R^4 , R^5 , R^6 , and R^7 react to 52 sulfuration ****, considering it as dithiophosphate, and neutralizing this with a zinc oxide. It cannot be overemphasized that structure of the above-mentioned dithiophosphate zinc changes with raw material alcohol to be used.

In a lubricating oil used for this invention, two or more sorts of dithiophosphate zinc included by the above-mentioned general formula (3) can also be mixed and used at an arbitrary rate.

[0043]

As mentioned above, a lubricating oil composition used for this invention shows the extremely outstanding low friction characteristic, when it uses for a sliding surface with a member which comprises a hard carbon film member, a charge of an iron substrate, or an aluminum material, but. In order to improve performance required especially as an internal-combustion-engine-oil constituent A metal system cleaning agent, An antioxidant, a viscosity index improver, other ash-free friction modifiers, non-[other] ash powder medicine, a wear inhibitor or an extreme pressure agent, a rust-proofer, a non-ion system surface-active agent, a demulsifier, a metal deactivator, a defoaming agent, etc. can be blended combining independent or two or more sorts, and required performance can be improved.

[0044]

As the above-mentioned metal system cleaning agent, arbitrary compounds usually used can be used as a metal system cleaning agent for lubricating oils. For example, sulfonate of an alkaline metal or alkaline-earth metals, phenate, salicylate NAFUTENETO, etc. can be used combining independent or two or more sorts. Here, as the above-mentioned alkaline metal, calcium (Ca), magnesium (Mg), etc. can be illustrated as the above-mentioned alkaline-earth

metals, such as sodium (Na) and potassium (K). As a concrete good example, sulfonate of Ca or Mg, phenate, and salicylate are mentioned.

The total basicity and an addition of these metal system cleaning agent can be arbitrarily chosen according to performance of a lubricating oil demanded. Usually, the total basicity is 150 - 400 mgKOH/g desirably zero to 500 mgKOH/g in a perchloric acid method, and the addition is a constituent whole-quantity standard, and is usually 0.1 to 10%.

[0045]

As the above-mentioned antioxidant, arbitrary compounds usually used can be used as an antioxidant for lubricating oils. For example, 4,4'-methylenebis (2,6-di-tert-butylphenol), Phenolic antioxidants, such as octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, Amine system antioxidants, such as phenyl-alpha-naphthylamine, alkylphenyl alpha-naphthylamine, and alkyl diphenylamine, a mixture concerning these arbitrary combination, etc. are mentioned. An addition of this antioxidant is a constituent whole-quantity standard, and is usually 0.01 to 5%.

[0046]

As the above-mentioned viscosity index improver, specifically, What is called non-distributed viscosity index improvers, such as a copolymer, its hydrogenation thing, etc. of one sort chosen from various methacrylic acid ester or two sorts or more of monomers, what is called a distributed viscosity index improver to which copolymerization of the various methacrylic acid ester which contains a nitrogen compound further was carried out, etc. can be illustrated. As an example of other viscosity index improvers, Non-distributed type or a distributed ethylene-alpha olefin copolymer (as alpha olefin) For example, the hydride and polyisobutylenes, such as propylene, 1-butene, and 1-pentene, and a hydrogenation thing of those, a styrenediene hydrogenation copolymer, a styrene maleic-anhydride-ester copolymer, poly alkyl styrene, etc. can be illustrated.

A molecular weight of these viscosity index improvers needs to select in consideration of shear stability. Specifically a number average molecular weight of a viscosity index improver, distributed type and non-distributed polymethacrylate -- 5000-1 million -- 100000-800000 being good and preferably, polyisobutylene or its hydride -- 800-5000, an ethylene-alpha olefin copolymer, or its hydride -- 800-300000 -- 10000-200000 are preferably good. As for the content, although this viscosity index improver can be made to contain combining independent or two or more sorts arbitrarily, it is usually desirable that it is 0.1 to 40.0% on a lubricating oil composition standard.

[0047]

As other ash-free friction modifiers, metal system friction modifiers, such as ash-free friction modifiers, such as the ester of boric acid, higher alcohol, and aliphatic series ether, dithiophosphate molybdenum, molybdenum dithiocarbamate, and molybdenum disulfide, etc.

are mentioned again.

Those derivatives, such as polybutenyl succinimid in which polybutenyl benzylamine, polybutenyl amine, and a number average molecular weight in which a number average molecular weight has a polybutenyl group of 900-3500 have less than 900 polybutenyl group as other non-ash powder medicine, are mentioned.

As the above-mentioned wear inhibitor or an extreme pressure agent, disulfide, sulfurized oil fat, olefin sulfide, phosphoric ester containing 1-3 hydrocarbon groups of the carbon numbers 2-20, thiophosphoric ester, phosphite, thiophosphite, these amine salt, etc. are mentioned.

As the above-mentioned rust-proofer, alkyl benzene sulfonate, dinonylnaphthalene sulfonate, alkenyl succinate, multivalent alcohol ester, etc. are mentioned again.

As the above-mentioned non-ion system surface-active agent and a demulsifier, polyalkylene glycol system non-ion system surface-active agents, such as polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, and polyoxyethylene alkyl naphthyl ether, etc. are mentioned.

As the above-mentioned metal deactivator, imidazoline, a pyrimidine derivative, thiadiazole, benzotriazol, thiadiazole, etc. are mentioned.

Silicone, fluorosilicone, fluoro alkyl ether, etc. are mentioned as the above-mentioned defoaming agent again.

In making the above-mentioned lubricating oil composition contain these additive agents, The content is a constituent whole-quantity standard, and can be suitably chosen [demulsifier / other friction modifiers, other non-ash powder medicine, a wear inhibitor or an extreme pressure agent, a rust-proofer, and / metal deactivator] from 0.0005 to 1% of range about a defoaming agent 0.005 to 1% 0.01 to 5%.

[0048]

[Example]

Hereafter, although an example and a comparative example explain this invention still more concretely, this invention is not limited only to these examples.

[0049]

(Production of a block)

The block as a slide member from ATAC86 treatment material and the hardening tempering material of the machinery structural carbon steel S45C. After starting in 10mm(stroke direction) x10mm(width) x5mm (thickness) shape, A 10-micrometer [in height] and pitch 200micrometer striation is formed in a stroke direction and the direction which makes a right angle, Spray coating of each resin material besides dissolved in the solvent was carried out so that the thickness after membrane formation might be set to 7-10 micrometers, the interlayer was formed, and the DLC film as a hard carbon film was further formed in thickness of 1 micrometer with plasma CVD method on this. And in some examples, the 2nd layer (outermost

superficial layer) that comprises DLC material with the PVD method by magnetron sputtering on it further in order [of the DLC film by the plasma CVD method concerned] to lessen a water content quantum was formed in thickness of 0.3 micrometer.

It substituted by sticking on the above-mentioned block raw material what formed the 10-micrometer-high striation in these surfaces directly, without performing the above spray painting, when fluorocarbon rubber and PEEK are used as an interlayer.

[0050]

(Production of plate material)

What ground the surface to Ra:0.3micrometer as plate material used as the mating material of the above-mentioned block slide member after starting in 60mm(stroke direction) x40mm (width) x10mm (thickness) shape from cast iron FC25 material, After starting in the same size from aluminum material A390 material and grinding the surface to less than Ra:0.1micrometer, what projected and processed primary phase Si from the aluminum-alpha phase to about 5 micrometers by the etching process was used.

[0051]

(Test method)

The friction wear test of the type which carries out both-way sliding of the above-mentioned plate material top whose above-mentioned block as a sliding part agent is a mating member in a sliding direction receiving fixed load was chosen as a valuation method. As a lubricating method, the fuel level of the lubricous oil bath was set as the position 3 mm before the bottom dead point (upper part) in up-and-down sliding of a block, and it was considered as the method which supplies lubrication oil to a sliding surface by dragging oil up at the time of the clinch in a bottom dead point.

The test condition is as follows and used the trial production lubricating oil which changed the additive agent and addition of commercial engine-oil 5W30SH for cars, and the 5W30SH concerned as a lubricating oil. The test result is shown in Table 1 with the specification of a block and plate material.

Test method; vertical mold reciprocation type friction wear test

Stroke: 40 mm

Pressing load: 100kgf

Test time: 60 minutes

Cycle: 1500 cpm

Oil temperature: 80 **

Coefficient of friction: Average value of one cycle

[0052]

[Table 1]

| 区分 | ブ ロ ッ ク (摺動部材) | | | | プレ ート 素材 | 潤 滑 油 | | | 評 価 結 果 | | | |
|-------|----------------|--------|----------|------------------------|-----------------|---------|--------|-------------|------------------|---------------------------|--------|------|
| | 基材 | 中 間 層 | | 硬質炭 素被膜 | | べー ス | 区 分 | 添 加 剤 | 摩 擦 係 数 | 摩 耗 量 (μ m) | 備 考 | |
| | | ゴム又は樹脂 | 添 加 剤 | | | | | | | | | |
| 実 施 例 | 1 | AC8A | ポリアミドイミド | — | CVD 膜 | FC25 | 5W30SH | 市販油 | | 0.06 | 0 | |
| | 2 | AC8A | ポリイミド | — | CVD 膜 | FC25 | 5W30SH | 試作油 | 脂肪酸エステル | 0.05 | 0 | |
| | 3 | AC8A | PEEK | — | CVD 膜 | FC25 | 5W30SH | 市販油 | | 0.06 | 0 | |
| | 4 | AC8A | フッ素ゴム | — | CVD 膜 | FC25 | 5W30SH | 市販油 | | 0.06 | 0 | |
| | 5 | AC8A | ポリアミドイミド | MoS ₂ | CVD 膜 +PVD 膜 | FC25 | 5W30SH | 試作油 | 脂肪酸エステル 脂肪酸7シ | 0.03 | 0 | |
| | 6 | S45C | ポリアミドイミド | PTFE, MoS ₂ | CVD 膜 +PVD 膜 | A390 | 5W30SH | 市販油 | | 0.05 | 0 | |
| 比 較 例 | 1 | AC8A | ポリアミドイミド | MoS ₂ | — | FC25 | 5W30SH | 市販油 | | 0.07 | 3 | |
| | 2 | AC8A | ポリイミド | — | — | FC25 | 5W30SH | 市販油 | | 0.12 | 5 | |
| | 3 | AC8A | PEEK | — | — | FC25 | 5W30SH | 市販油 | | 0.14 | >10 | 条痕摩耗 |
| | 4 | AC8A | ポリアミドイミド | — | — | FC25 | 5W30SH | 試作油 | 脂肪酸エステル | 0.10 | 5 | |
| | 5 | AC8A | なし | — | — | FC25 | 5W30SH | 市販油 | | 0.14 | 3 | |
| | 6 | S45C | ポリアミドイミド | PTFE, MoS ₂ | — | FC25 | 5W30SH | 市販油 | | 0.08 | 3 | |

[0053]

In the block concerning the example of this invention which gave covering which consists of hard carbon thin films on the interlayer who comprises resin etc., wear was hardly accepted but survival of the striation was checked on the hard carbon coat even after test termination so that clearly from the result shown in Table 1. And the low friction effect was acquired by blending oil pharmaceutical preparation, such as ester, into a lubricating oil, and it was checked by forming the hard carbon film of low-water-flow matter content by the PVD method that the still more remarkable low friction effect is acquired.

The lubricative aggravation accompanying wear of a striation was accepted by each in the comparative example block with which the hard carbon film is not given on the other hand on the interlayer who comprises resin etc. Although some improving tendency was accepted by the solid lubricant addition to a resin layer, it was less than the example which gave hard carbon covering.

[0054]

[Effect of the Invention]

As explained above, according to the hard carbon film slide member of this invention which gave hard carbon covering of DLC material etc. to the sliding surface of the substrate which comprises a steel material and an aluminum material via the elastic interlayer who consists of rubber, resin, etc. The outstanding effect that the coefficient of friction and abrasion loss as a slide member can be decreased substantially is brought about by existence with the hard carbon film of the interlayer excellent in elasticity, and the outermost superficial layer which is excellent in abrasion resistance and has the low friction characteristic.

[Translation done.]